## Surfaces, Interfaces, Spins - The age of Interface!

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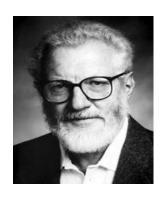
#### Why interface is important?

#### "The interface is the device"

- Herbert Kroemer

#### Interface is the platform for creating exotic electronic states:

- Semiconductor heterostructure interface: (electronelectron interaction) high mobility electron gas, fractional charge and statistics, topological order etc.
- Oxide heterostructure interface: (correlated electrons)
   high mobility electron gas, ferroelectricity, high temperature superconductivity etc.
- **Topological insulator surface**: (*spin-orbit coupling*) topological surface states
- Combined interactions: ferromagnetic, superconductivity, spin-orbit etc.
   → exotic electronic state: Majorana fermion



Herbert Kroemer

Nobel Prize in Physics (2000)

"for developing semiconductor heterostructures used in highspeed- and opto-electronics"

Nobelprize.org

#### Postdocs: Ferhat Katmis, Peng Wei, CuiZu Chang Yunbo Ou, Juanpedro Cascales

**Visiting Scientist: Yota Takamura** 

#### **Collaborators**

```
mK transport - W.W. Zhao, .... J. Jain and M. Chan - Penn State
PNR - Valeria Lauter - Oakridge Natl Lab
SQUID - Don Heiman - Northeastern U
XAS, XMCD - John Freeland - Argonne Natl Lab
```

XTEM - Biswarup Satpathy - Saha Inst. Nucl. Physics, India

TIG/TI - Chi Tang, Jing Shi - U of California Riverside

Theory - Kyungmin Lee, Nandini Trivedi - Ohio State U.

- Spins Spintronics: unconventional
- Spins Superconductors
- Spins Quantum coherent systems

The common platform

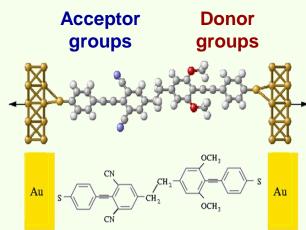
- surfaces and interfaces!!

#### **Towards Molecular Spintronics**

#### Why single molecules?

- Smallest well defined electronic units
- Chemically synthesize precisely designed properties, with atomic precision tune tailored molecules!
  - ..... Unlimited possibilities ....
- Easily scalable

Add: electron spin degree of freedom for spintronic functions within single molecular building block

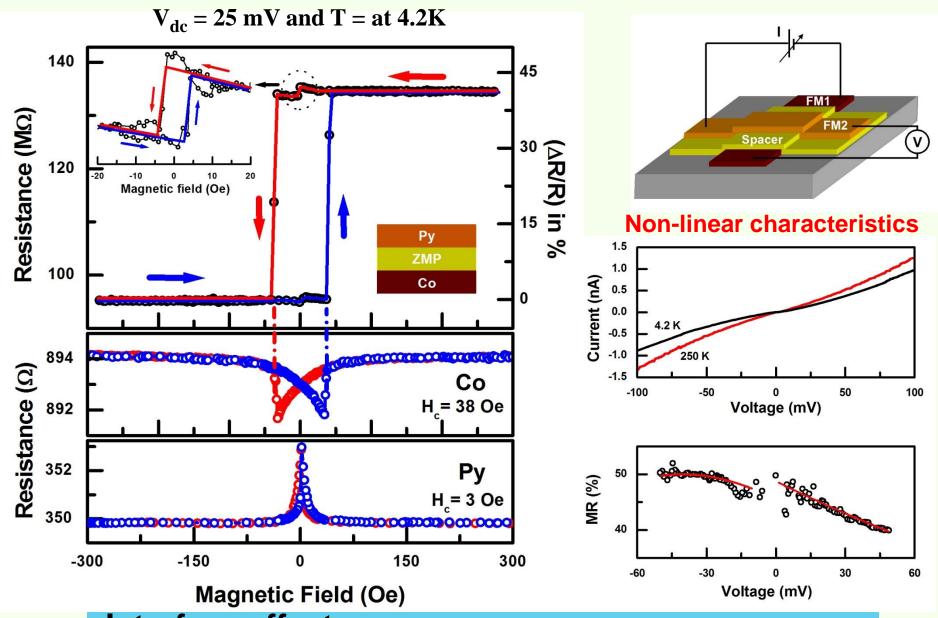


Molecular rectifier Aviram and Ratner, (1974).

Towards single molecule information storage and sensing

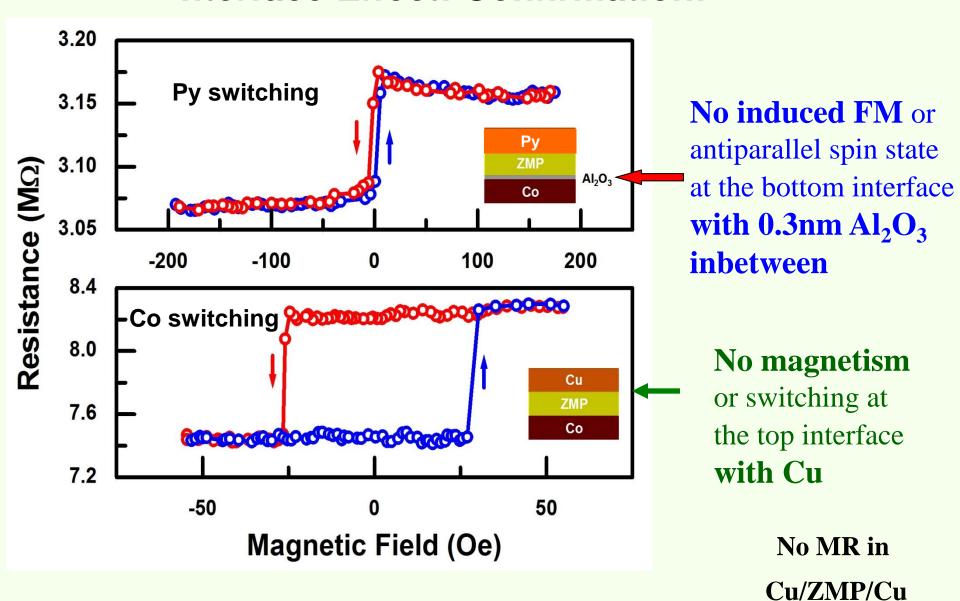
We are at the beginning  $\rightarrow$  Need of basic research!

#### Magnetoresistance in Co/ZMP (40 nm)/Py spin valve



Interface effect: K. V. Raman ..... JSM, Nature 493, 509 (2013)

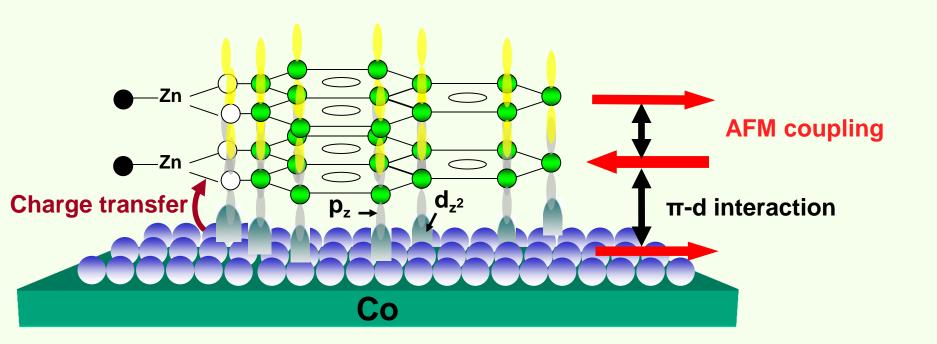
#### **Interface Effect: Confirmation!**



A 'pinned magnetic layer' exists at the interface

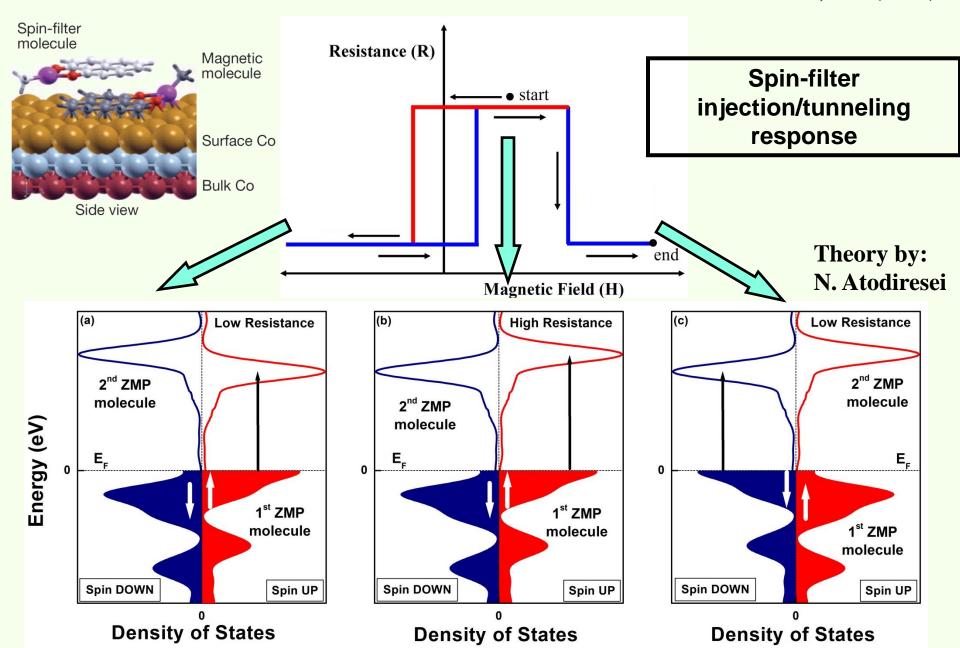
#### Interface phenomena

#### Zinc methyl phenalenyl molecules over Co surface



#### **Origin of IMR effect**

Raman et al. Nature 493, 509 (2013)



#### Towards molecular spintronics .....

- planar organic molecules (ZMP)
  - → magnetic & spin-filtering room temperature
- Molecules can store information as a classical bits i.e. '0' or '1' state
   Storage density may reach ~ 1000 TBytes/sq inch

#### Technological advantages ...

Only one FM needed

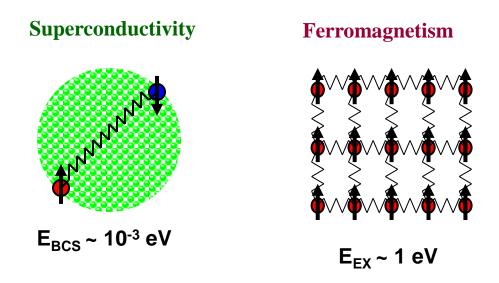
Molecular 'bit' - integrated storage-sensing system

Molecules are ideal quantum dot systems

- fabrication of scalable quantum memory registers

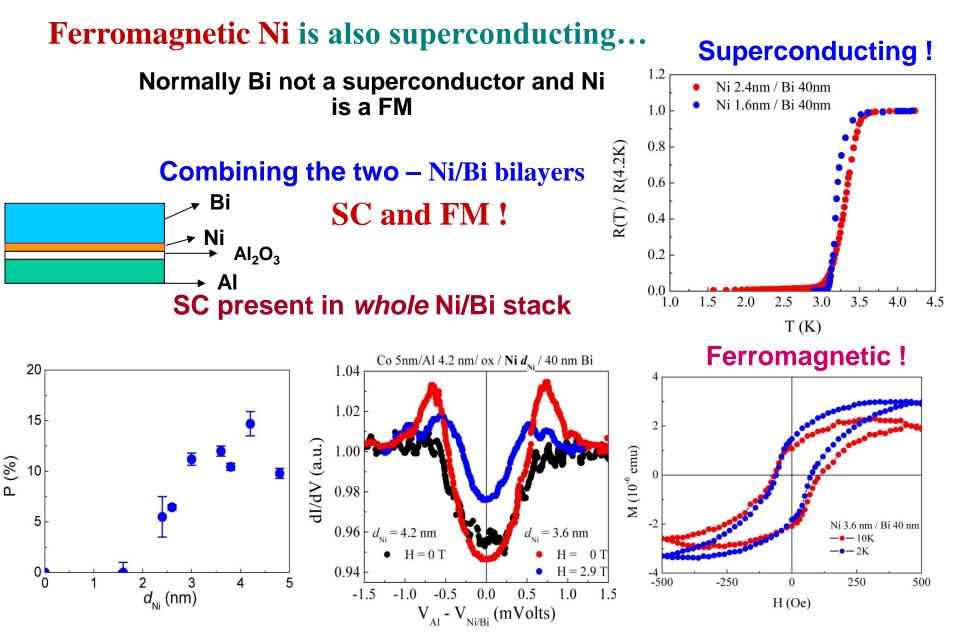
#### Coexistence of

#### Superconductivity and Ferromagnetism!!



SC and FM are competing spin ordering mechanisms

An unexpected observation ....
Ferromagnetic Ni is superconducting !!



Superconductivity and ferromagnetism coexist in Ni !!

Spin polarized current observed in a triplet SC?!

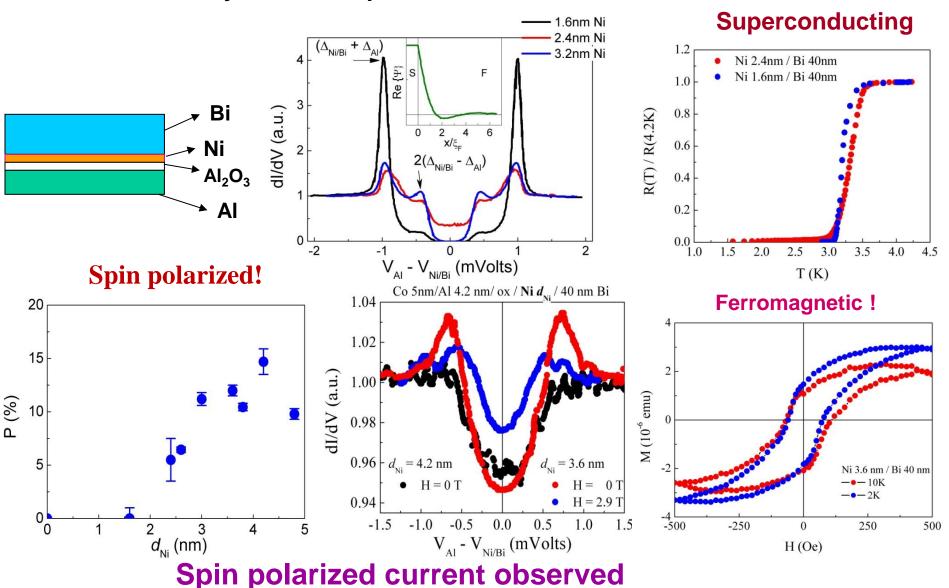
PRL 92

PRL 94, 037006 (2005)

#### Superconductivity and ferromagnetism coexist in Ni/Bi bilayers !!

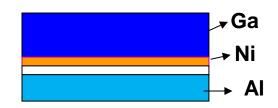
Normally Bi not a superconductor and Ni is a FM

- triplet paired SC?!



PRL 94, 037006 (2005)

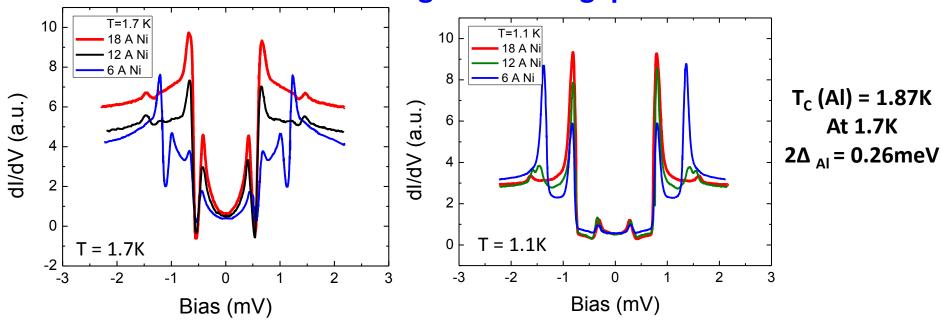
Bulk Ga Tc = 1.08K amorp Ga Tc = 8.6K, only stable < 20K



#### X Ni/600A Ga film – superconducts with Tc ~ 6.5K

3-10057





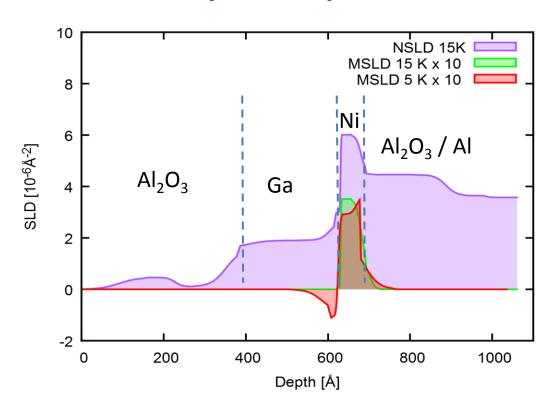
For 0.6nm Ni:  $2\Delta_{\text{Surface}} = 1.14 \text{meV}$ ;  $2\Delta_{\text{Interface}} = 2.28 \text{meV}$ ;  $2\Delta_{\text{Bulk}} = 2.76 \text{meV}$ 

For 2.4nm Ni:  $2\Delta = 0.45$ meV;  $2\Delta = 1.15$ meV;  $2\Delta = 2.70$ meV  $2\Delta/kT_c \sim 4.5 - strong coupled$ 

#### Polarized Neutron Reflectivity results for Ni 56 A / Ga 600 A

**At 5K Meissner state:** field from the Ni side is screened at the Ga interface

M profile: positive M in Ni; negative in Ga

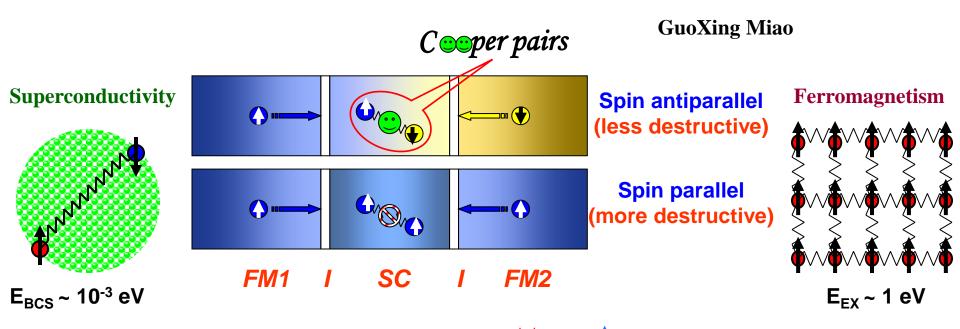


Samples zero field cooled to 15 K, H 1 kOe applied – measure PNR ZFC to 5 K H = -150 Oe applied H 1 kOe applied – measure PNR

40 and 56 A Ni show clear magnetic signature adjacent to 600A Ga which is superconducting

#### Tuning superconductivity with spin current ...

#### SC and FM are competing spin ordering mechanisms



Large MR is expected between ↑ and ↓ states

Reduced transparency:  $6 \text{ Fe} / 1 \text{ Al}_2\text{O}_3 / 4 \text{ Al} / 1 \text{ Al}_2\text{O}_3 / 6 \text{ Py} > 1000\% \text{ MR}$ 

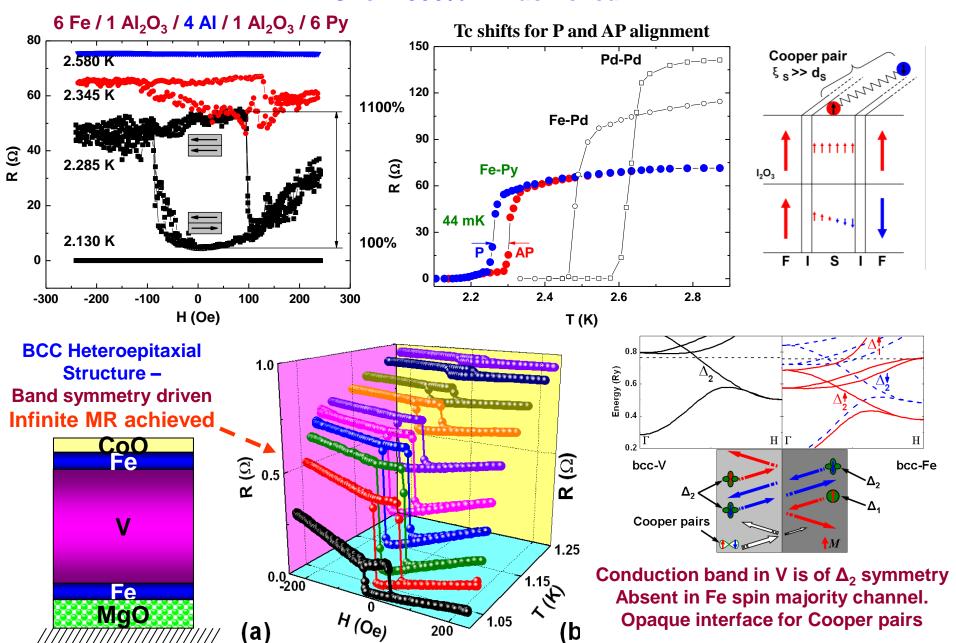
Transparent interface: Epitaxial 6 Fe / 40 V / 6 Fe/1 CoO – Infinite MR

PRL 2007, 2008

#### **Spin injection into superconductors**

Over 1000% MR achieved!!

PRL 2007, 2008



200

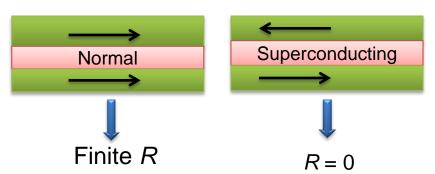
(a)

(b

#### De Gennes' prediction – 50 years ago

de Gennes, Phys. Lett. 23, 374 (1966)

Ferromagnetic Insulator
Superconductor
Ferromagnetic Insulator

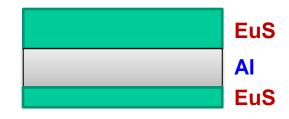


Average exchange field

$$\bar{h} = 2|\Gamma|S\left(\frac{a}{d_s}\right)\cos\frac{\theta}{2}$$

From Tc change - exchange integral

$$\Gamma = 8.1 \, meV$$



Average exchange field

$$\overline{h} \sim 13 \; meV$$

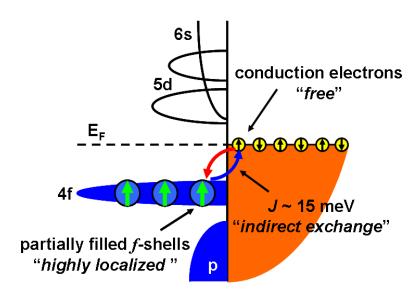
Shows perfect superconducting spin switching effect

Equivalent external field ~200 T

### Internal exchange field – Proximity effect at a ferromagnet insulator / metal interface

#### Magnetic semiconductors EuS or EuO

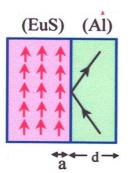
**Exchange Interaction between EuS** and normal metal



$$H_{EX} = -J\left(\overrightarrow{S_{e^{-}}} \cdot \overrightarrow{S_{Eu^{2+}}}\right)$$

Sarma 1963 de Gennes, 1966 Tedrow et al PRL 1986

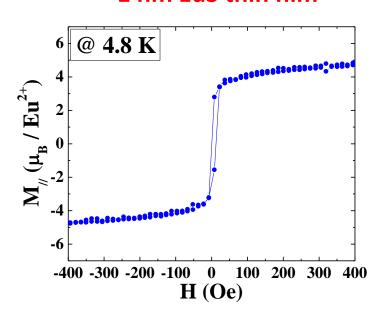
 $B^* \propto 1/d$ 



#### EuS Band gap $E_g = 1.64 \text{ eV}$ $\Delta E_{ex} = 0.36$

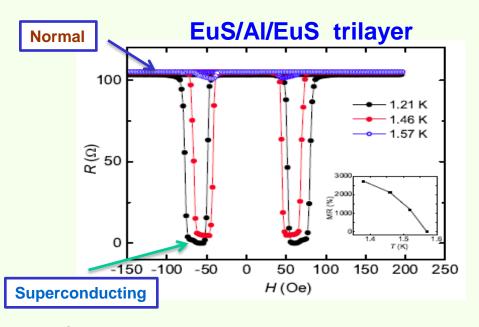
Magnetic Hysteresis

1 nm EuS thin film

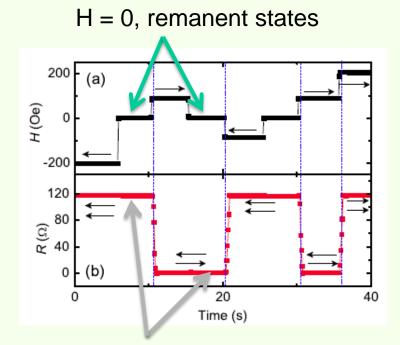


#### EuS/Al/EuS superconducting spin switch

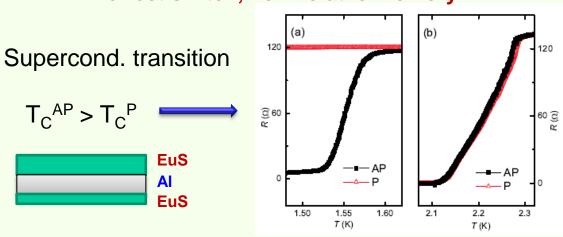
Li... JSM, PRL 2013

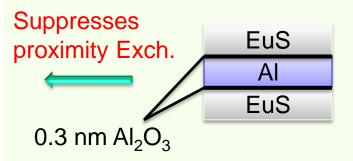


- Complete normal-superconducting transition
- Infinite magnetoresistance (MR) --Perfect switch, non-volatile memory

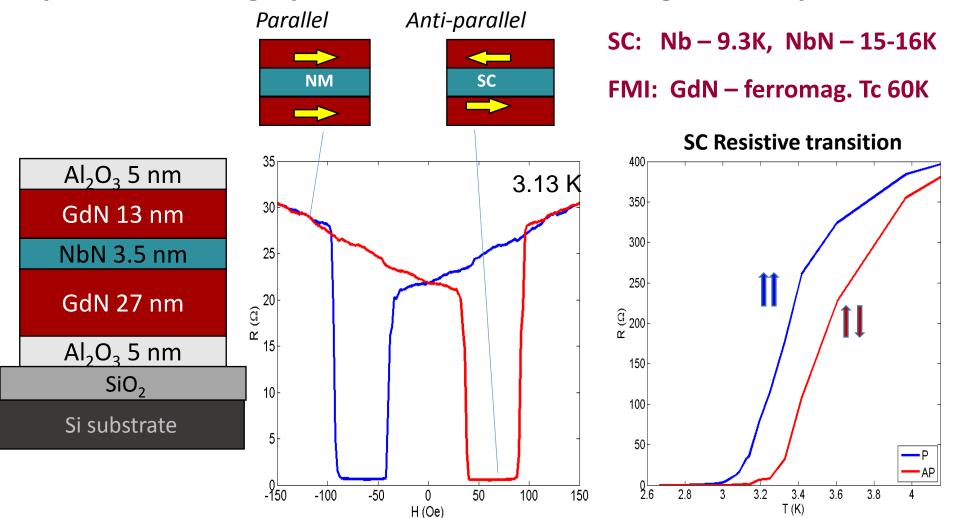


#### Two resistance states





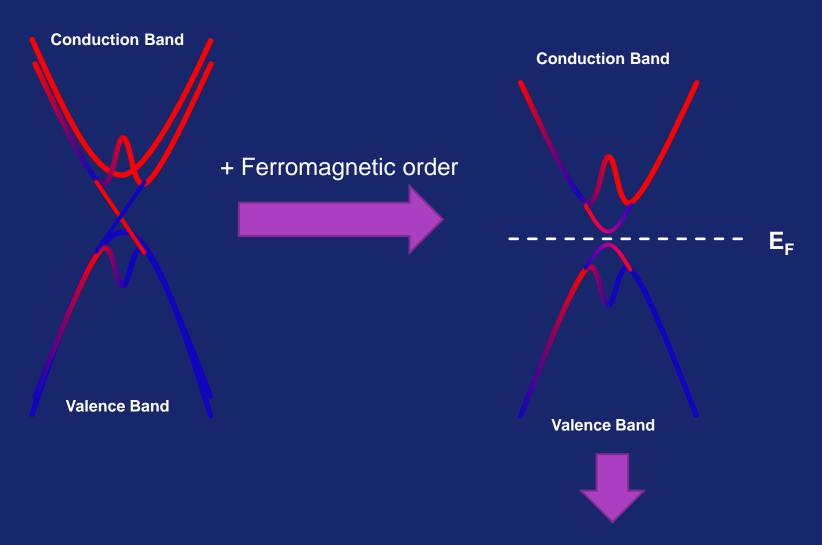
#### Superconducting Spin Switch realized at higher temperatures



Perfect spin switching Interface driven

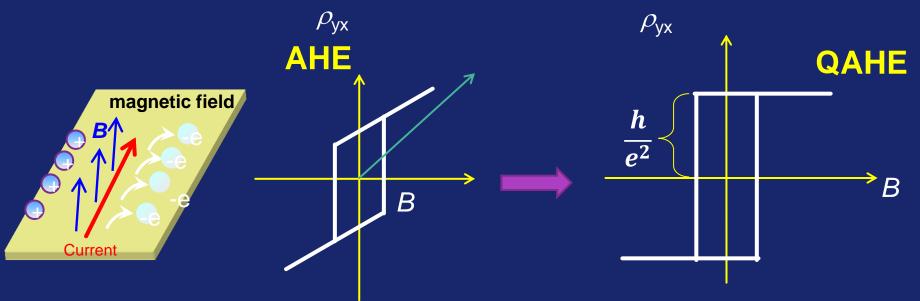
#### **Topological Insulators (TIs)**

#### Topping in the state of the sta



Quantum anomalous Hall (QAH) effect

#### Quantum anomalous Hall (QAH) effect



Hall effect at zero field in a magnetic material

Quantum Hall effect at zero field

- Ferromagnetic insulator
- Topologically non-trivial electronic band structures

$$\rho_{yx} = \frac{h}{e^2} = 25.812 \text{ K}\Omega$$

$$\rho_{\chi\chi}=0$$

Spin polarized ballistic chiral edge mode

**QAH** insulator

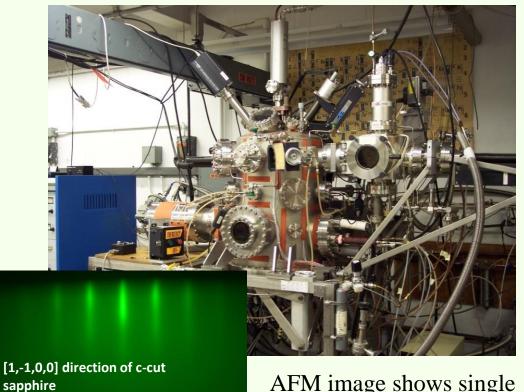
- TI thin films and heterostructures High quality
  - → Homogeneous composition
  - → Negligible defects
  - → High mobility and low carr. density

#### To reach QAH state

- Create ferromagnetic TI by doping
  - where does the dopant go?
- TI/FMI heterostructure
   Interface coupled magnetic behavior

#### **Epitaxial growth (MBE) of TI layers**

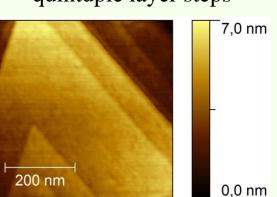
Bi<sub>2</sub>Se<sub>3</sub>

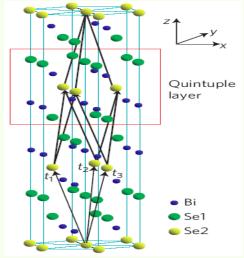


AFM image shows single quintuple layer steps

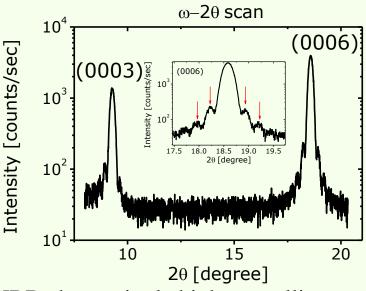
Layer by layer growth Insitu capping

Heterostruc. possible TI-I-Metal TI-SC TI-FMI



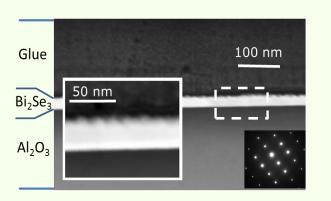


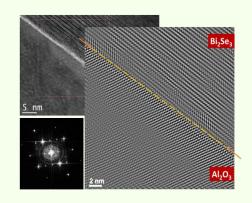
H. Zhang et al Nat Phys 5, 438 (2009)

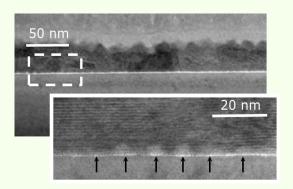


XRD shows single high crystalline quality and terraced surface 25

### - Dislocation mediated structural ordering - Signature of ordering, influence on carrier mobility

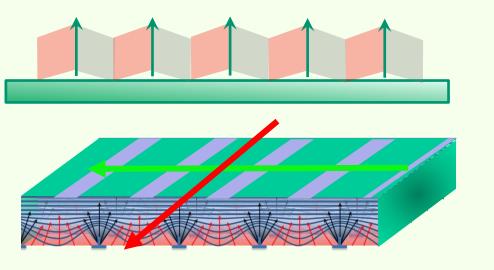


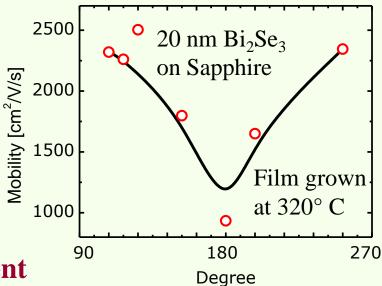




XTEM, STEM data very valuable

Strong structural anisotropy!



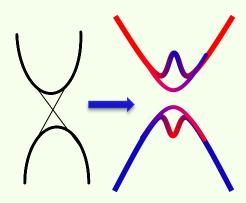


Mobility depends on the current

direction w.r.t. dislocation lines!

## To observe QAH state Create a ferromagnetic TI

- Surface Dirac cone opens up a gap ....



Control film thickness and carrier density to achieve QAHE

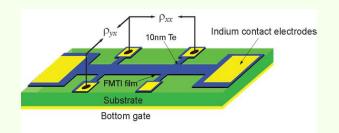
Doping TI with magnetic impurities: Cr, Mn, V etc.

Reduces surface mobility, spin disorder
Higher Tc requires high doping, lowering S-O - can destroys
nontrivial surface states

- Proximity driven: through internal exchange field with a magnetic insulator Independent optimization of elec. and mag. properties Could be a cleaner approach!

#### Ferromagnetism in Cr-doped Bi<sub>2</sub>Se<sub>3</sub> epitaxial films (2010-11)

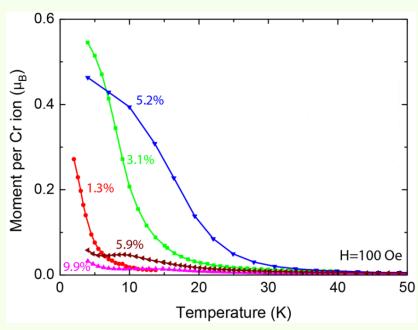
- Lattice parameter c increased (~0.2 %)
- Strain increased
- With increasing Cr concentration crystal/film quality decreased



#### **Anomalous Hall effect seen** T = 3.0K**60 30** $R_{\rm AH}\left(\Omega\right)$ 7.0K 60.0K -30 -60 30 -60 -30 **60** H (kOe)

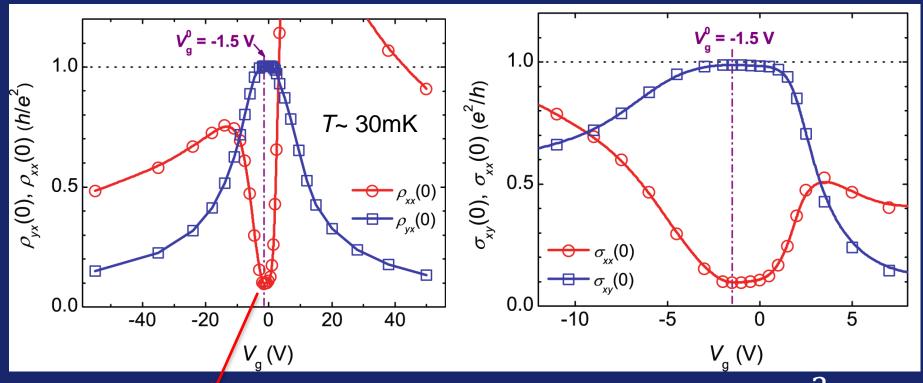
#### Film quality optimized: 5% Cr

#### Tc dependence on Cr content



P. P. J. Haazen, J. B. Laloe, P. Wei.... JSM, (2010, APL 2012)

#### QAHE in 5QL Cr-doped (Bi<sub>0.1</sub>Sb<sub>0.9</sub>)<sub>2</sub>Te<sub>3</sub> film - ferromagnetic TI



Not completely dissipationless

$$\rho_{xx} \sim 2.53 \text{K}\Omega$$

$$\rho_{yx} = 1 \frac{h}{e^2}$$

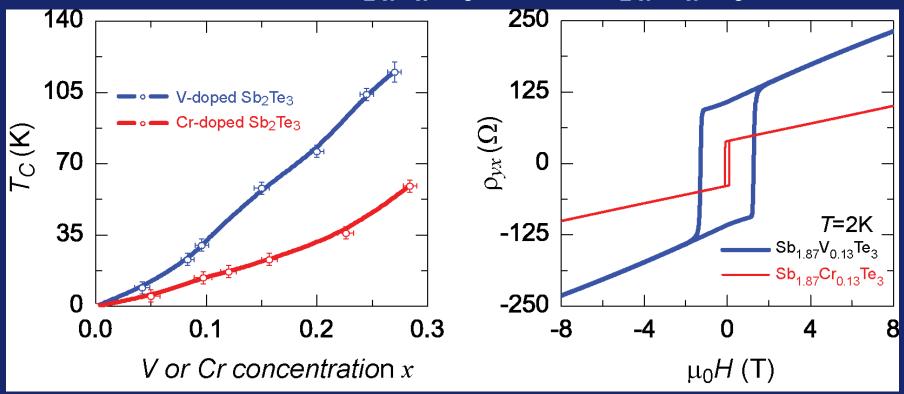
$$\sigma_{yx} \sim 0.99 \frac{e^2}{h}$$

$$\tan \alpha = \frac{\rho_{yx}}{\rho_{xx}} \sim 11$$

Chang et al. Science **340**,167 (2013).

## Ferromagnetic properties Comparing Cr- and V-doped Sb<sub>2</sub>Te<sub>3</sub> films

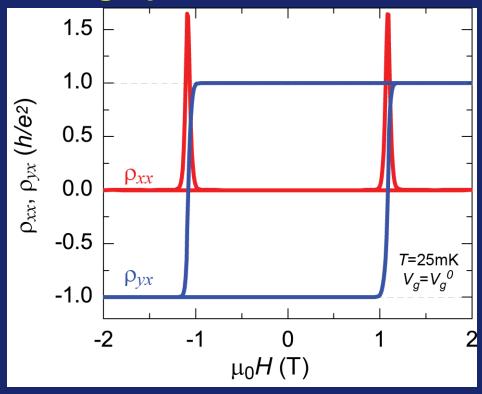
 $\overline{6 \text{ QL } \text{Sb}_{2-x}\text{V}_x\text{Te}_3}$  and  $\text{Sb}_{2-x}\text{Cr}_x\text{Te}_3$ 



 $Sb_{2-x}V_xTe_3$ : Higher Curie temp. Giant coercive field

Magnetic moment per V ion 1.5 µ<sub>B</sub> for x = 0.13
 valence state of V is a mixture of 3+ and 4+ (or/and 5+)
 reduces p-type carriers by n- doping

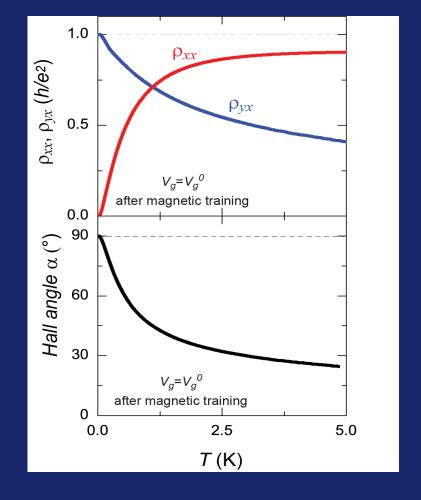
#### **High-precision QAHE**



At 
$$H = 0$$

$$ho_{yx}$$
=1.00019 $\pm$ 0.00069  $h/e^2$   
 $ho_{xx}$ = 0.00013 $\pm$ 0.00007  $h/e^2$  (~3.35 $\pm$ 1.76 $\Omega$ )

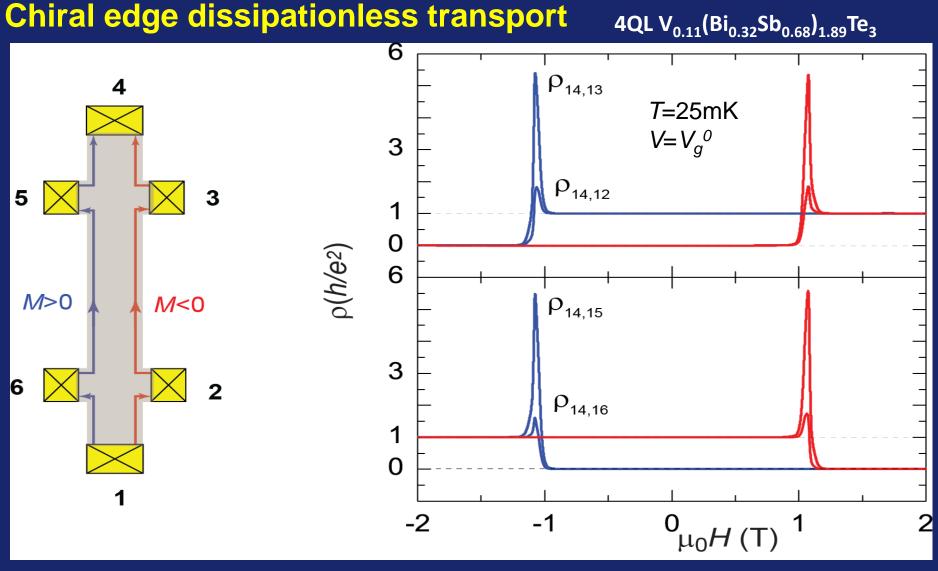
$$\rho_{vx}(0)/\rho_{xx}(0) \sim 7700 \quad \alpha \sim 89.993 \pm 0.004^{\circ}$$



$$\rho_{yx} = \frac{h}{e^2} = 25.812 \text{ K}\Omega$$

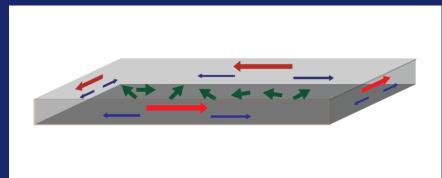
#### $\rho_{XA} = 0$ state up to ~5K

Nat. mater. 14, 473(2015)



Asymmetric loops PRL (2015) Mirror symmetric behavior of  $\rho_{14,16}$  ( $\rho_{14,15}$ ) and  $\rho_{14,12}$  ( $\rho_{14,13}$ ) The chirality of edge transport in QAH state

#### Complex - several conducting channels

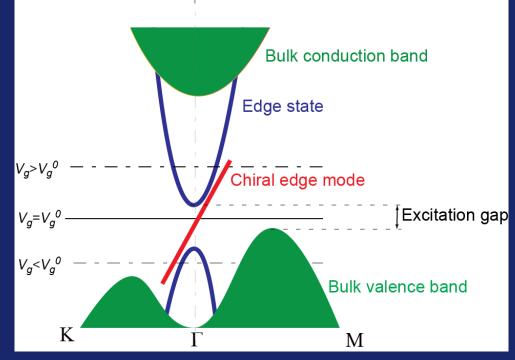


Red: Chiral edge mode

Blue: Nonchiral edge mode

Green: Bulk channels

Non-uniform exchange gap



$$V_g = V_g^0$$

Activation energy ~ 100 μeV

Chiral edge channel (red) (dissipationless)

$$V_g > V_g^0$$

Nonchiral edge channel (blue) (dissipative) + Chiral edge channel (red) (dissipationless)

$$V_q < V_q^0$$

Bulk channels (green) (dissipative) + Chiral edge channels (red) (dissipationless)

Phy. Rev. Lett. 115, 057206 (2015)

## Creating ferromagnetic state by proximity coupled interfacial exchange field

Ferromag. Insulator

Nonmagnetic layer

Interface
controls

#### Very effective with superconductors

PRL 1986, 1988, 1991, 1993, 2007, 2008, 2009;

Nat. Commun. 2014; PCCP 2015

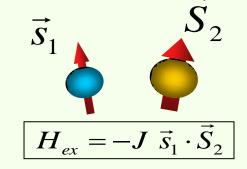
Nature 2016, Nature Matl. 2016

## Internal exchange field: Proximity induced surface ferromagnetism in TI

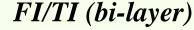
Large internal exch. field at FI/TI interface

> many Tesla

- Ferromagnetic Insulators (FI): EuS, Eu<sup>2+</sup> ion: 7  $\mu_B$
- 4f-5d energy gap: 1.64 eV (EuS) or 1.12 eV (EuO)
- Exchange interaction energy J ~ 15 meV



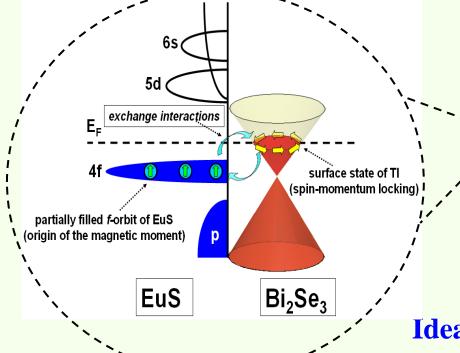
de Gennes 1966 Sarma 1963





**Split surface bands** (short range interaction)

Ideal for TI as interaction is at the surface



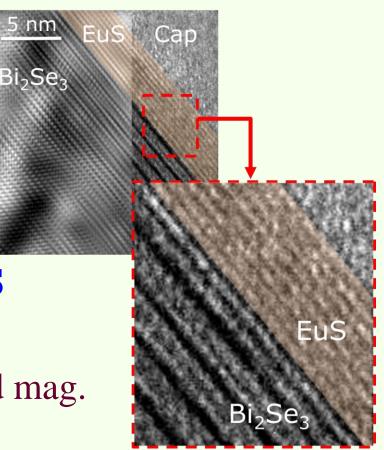
# Introducing ferromagnetism on TI surface via interfacial exchange fields Ferromagnetic Insulator / TI





Independent optimization of elec. and mag. properties

Could be a cleaner approach!

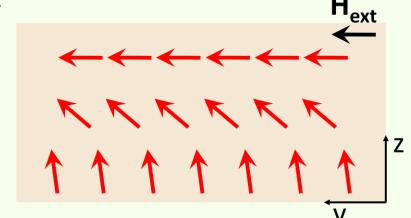


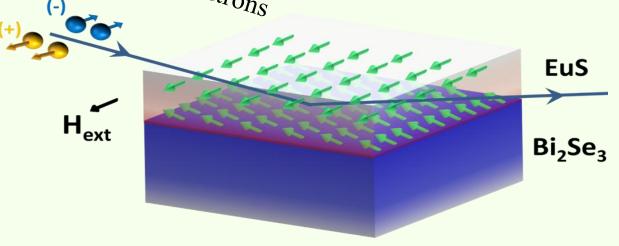
### **Polarized Neutron Reflectometer**

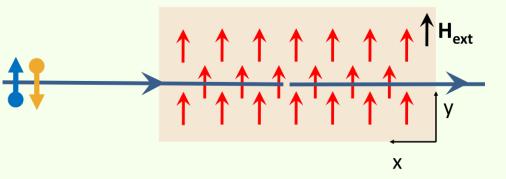
Oakridge Nat. Lab (Valeria Lauter)

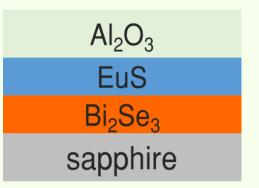
### **Probing the interface spins**

beam of spin
polarized neutrons



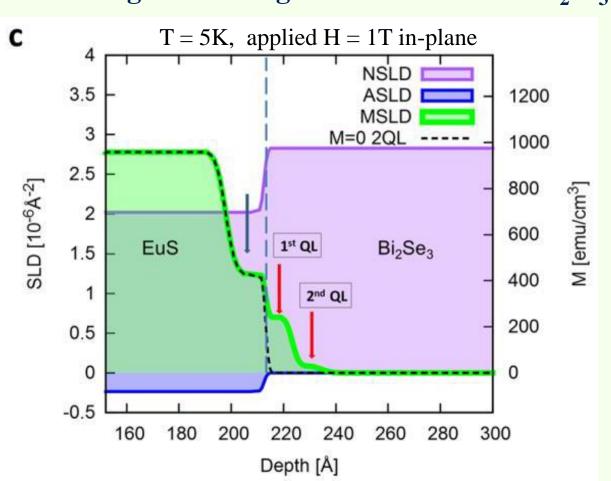






# **Interface layer ferromagnetism in TI**by Spin-Polarized Neutron Reflectivity

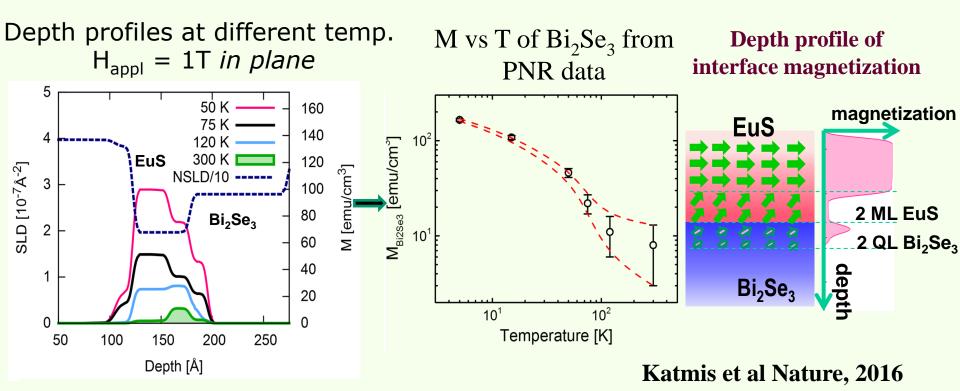
### PNR signal showing induced M in EuS/Bi<sub>2</sub>Se<sub>3</sub>



# Depth profile of the interface magnetization EuS magnetization 2 ML EuS 2 QL Bi<sub>2</sub>Se<sub>3</sub> Bi<sub>2</sub>Se<sub>3</sub>

F. Katmis .... JSM, Nature, 2016

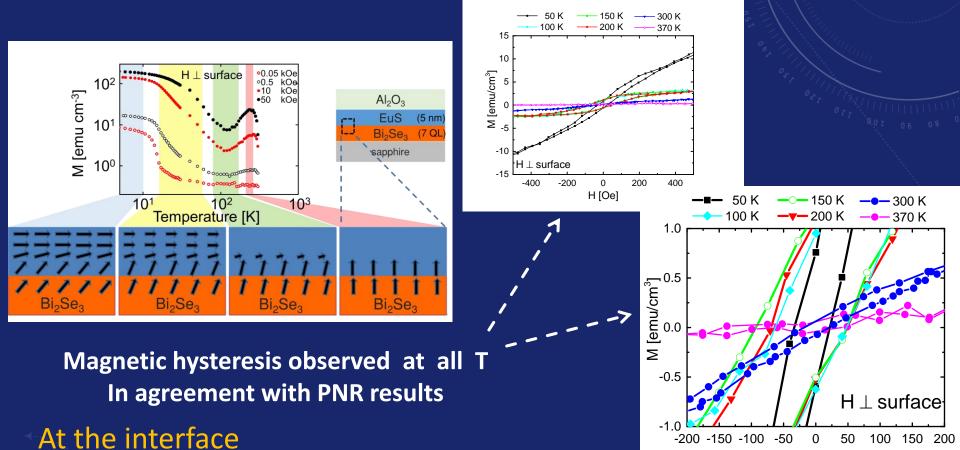
### Polarized Neutron Reflectometer: Bi<sub>2</sub>Se<sub>3</sub>/EuS (10 QL / 5 nm)



- High quality thick EuS layer magnetization confirmed by PNR (~7m<sub>B</sub> per Eu<sup>2+</sup> ion)
- Canted interface EuS moment (planar ~  $0.3m_B/Eu^{2+}$ , corresponds to ~  $85^{\circ}$  canting angle)
- Onset of large induced moment within the top 1-2 QL Bi<sub>2</sub>Se<sub>3</sub>, decays with depth
- No induced interface moment seen in control sample of EuS/sapphire

### SQUID MAGNETOMETRY MEASUREMENT

Magnetization vs. Temp. at various perpendicular applied fields



 Large S-O interaction, the spin-momentum locking at Dirac surface state creates strong anisotropy and stabilizes the ferromagnetic state?!

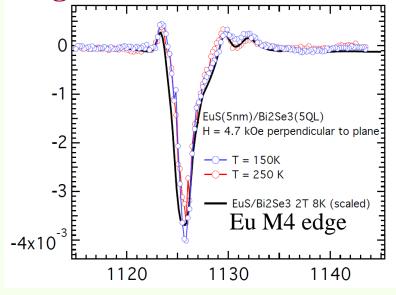
H [Oe]

Electron density profile of EuS/Bi<sub>2</sub>Se<sub>3</sub> bilayer (glancing angle XRD analysis, synchrotron source used)

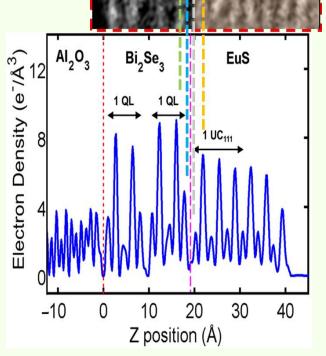
• Bi<sub>2</sub>Se<sub>3</sub> is terminated with Se layer at the interface; S layer is in direct stacking with Se layer

- Agrees with TEM analysis
- Sharp interface, no intermixing or inter diffusion
- Weak interfacial bonding van der Waals bond (~ 2.45 Å)

Magnetic circular dichroism vs. Temp.



~ 0.05 - 0.1 uB per atom at 250K



~ 2.45 Å

Eu

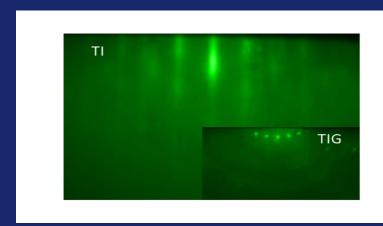
Bi

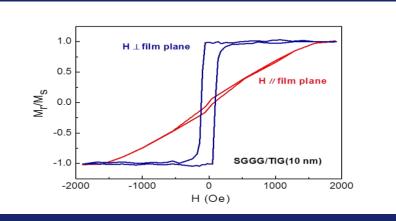
 $EuS/Bi_2Se_3$  interface layer shows ferromag. behavior at  $250K >> T_C(EuS)$ 

# .... Going to higher temperature .... TI/TIG heterostructure (Collab: Jing Shi, UC Riverside)

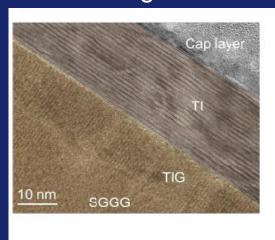
RHEED patterns of TI/TIG

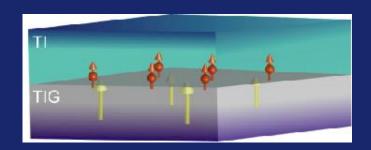
M-H loop of TIG substrate

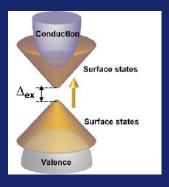




### TEM image of TI/TIG



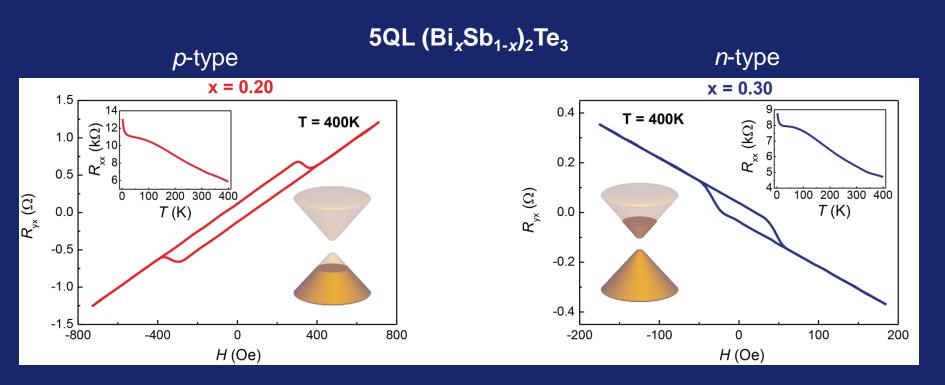




 $T_c \sim 560 \text{K} \longrightarrow \text{Large exchange-induced gap}$ Science Advances (Online June 2017)

### Hall traces of TI/TIG heterostructure

Science Advances (Online June 2017)

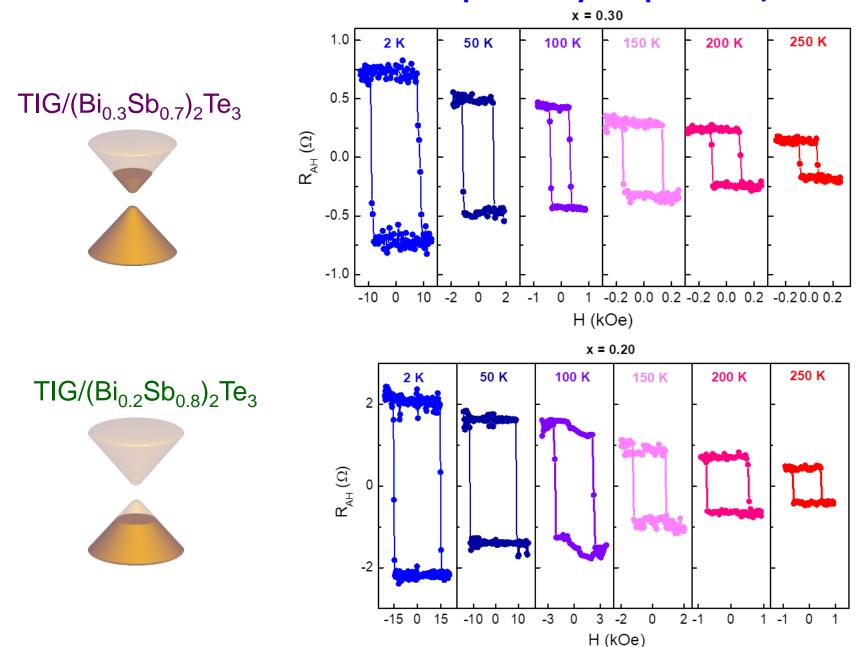


The AHE loops have the same sign in these two samples despite the different carrier types

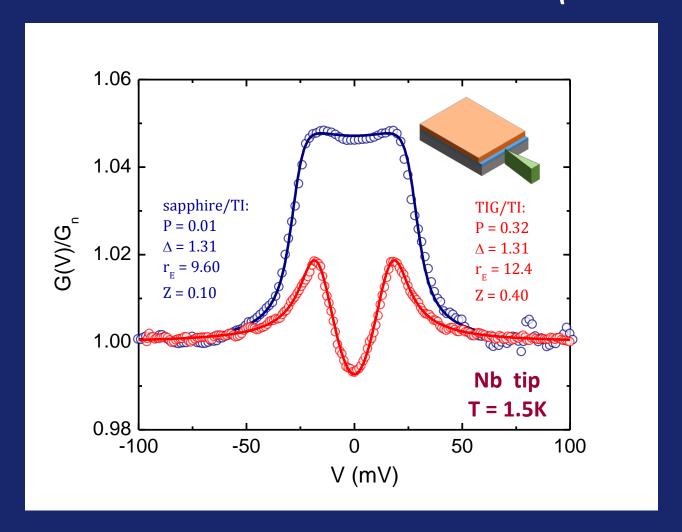


NOT Lorentz force-induced responses arising either from TIG stray fields or contributions from two types of carriers in TI

### Anomalous Hall resistance in proximity coupled TIG/ 5QL TI



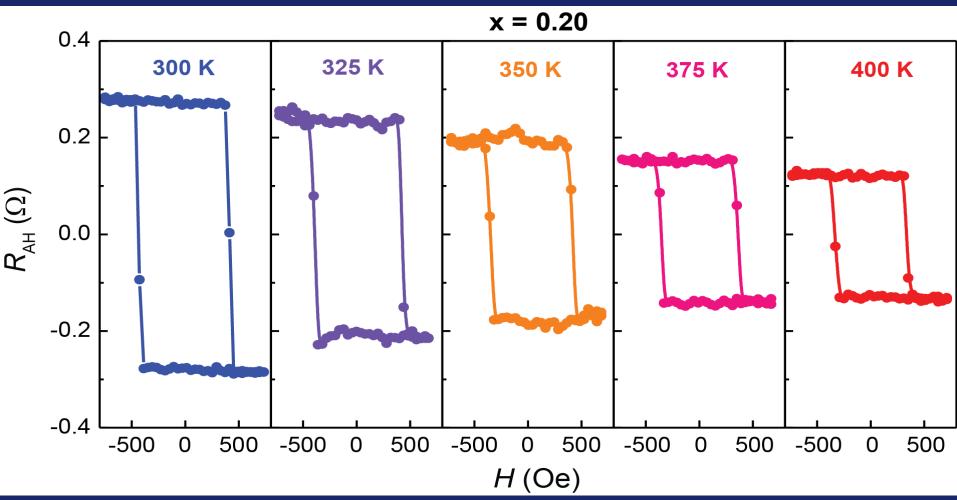
# Point-contact Andreev reflection spectroscopy (PCAR) on TI/TIG heterostructure Science Advances (Online June 2017)



Spin polarization at the interface of TI/TIG heterostructure, indicates the interfacial induced FM phase in TI

### Temperature dependence of AHE response in TI/TIG

5QL  $(Bi_xSb_{1-x})_2Te_3$  *p*-type

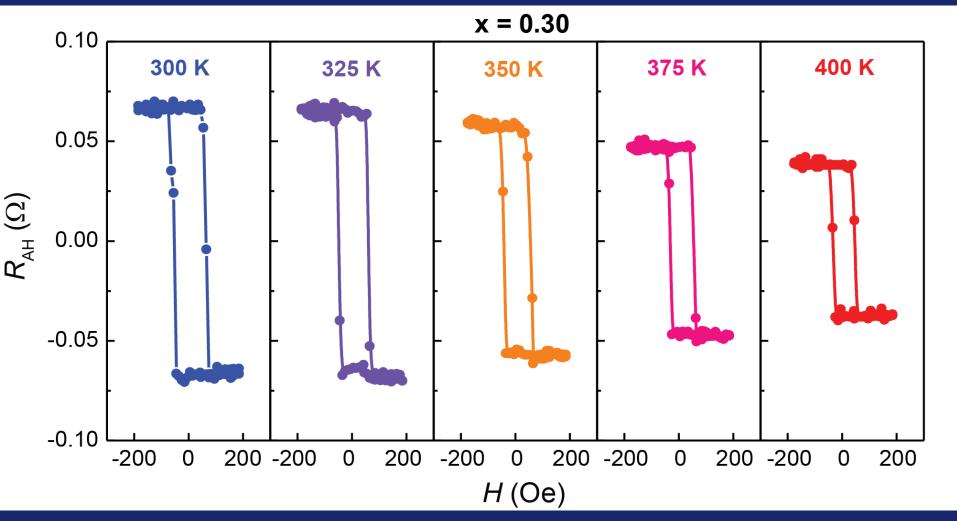


- Perpendicular FM phase exists throughout the entire temperature range up to 400 K
- AHE resistance increase with decreasing the temperature

### Temperature dependence of AHE response in TI/TIG

 $5QL (Bi_xSb_{1-x})_2Te_3$ 

*n*-type



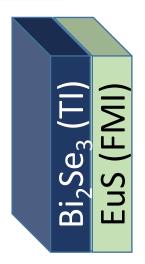
- Perpendicular FM phase exists throughout the entire temperature range up to 400 K
- AHE resistance increase with decreasing the temperature

### **Heterostructure FMI/TI bilayer**

- magnetic order by surface states

### (Kyungmin Lee, Nandini Trivedi) **Ohio State Univ.**

### Model:



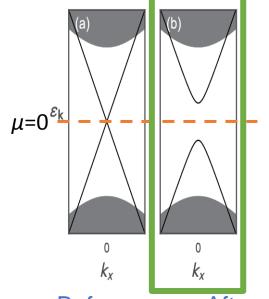
Kondo coupling between spin and surface state

$$\mathcal{H}_{\text{Kondo}} = J \sum_{\mathbf{x}} \mathbf{S}(\mathbf{x}) \cdot c_{\mathbf{x}}^{\dagger} \boldsymbol{\sigma} c_{\mathbf{x}}$$

generates effective spin-spin interaction through RKKY-like mechanism

Effect of FMI on

TI: Gapping of topological surface states of TΙ



Before coupling

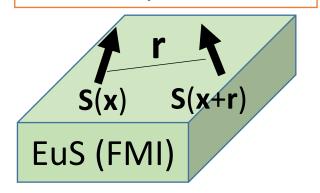
**GAPLESS** 

After coupling to

to FM: FM: Massive Dirac

Effect of TI on FMI: Additional exchange

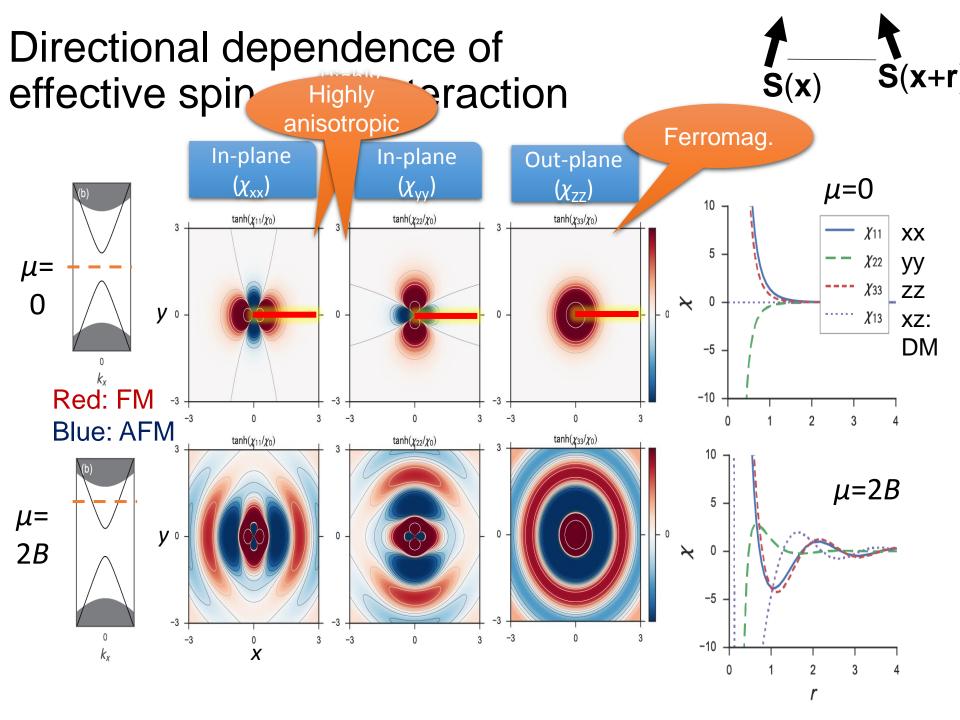
and DM coupling generated between classical spins



$$\delta F_2[\mathbf{S}] = -J^2 \sum_{\mathbf{x}, \mathbf{y}} S_i(\mathbf{x}) S_j(\mathbf{y}) \chi_{ij}(\mathbf{x} - \mathbf{y})$$

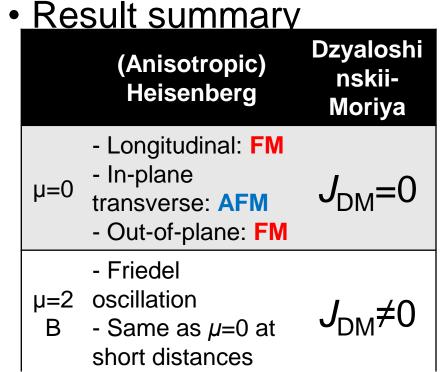
$$\widetilde{J}_{ij}(\mathbf{r}) = -J^2 \chi_{ij}(\mathbf{r})$$

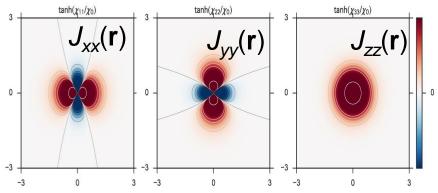
χ: spin-spin correlation of surface states



### Results for effective spin-spin interaction

- Effective spin interaction in FM mediated by the TI surface states can enhance  $T_{\rm C}$ .
- Spin-momentum locking of surface state → highly anisotropic spin interaction (RKKY of spin-degenerate metal is isotropic)
- "Frustrated" in-plane vs. stable ferromagnetic out-of-plane interaction
  → consistent with out-of-plane magnetism at interface exptl. obser.
- Oscillation in spin interaction as function of distance → Possibly sensitive to lattice constant change
- Both Heisenberg and Dzyaloshinskii-Moriya present → Possible skyrmion phase(?)





## Summary

# Investigating TI quantum properties REQUIRES high quality TI films and heterostructures

- Ferromagnetic TI transition metal doped
   QAH state obtained
   Chiral dissipationless edge conduction observed
- TI proximity coupled to ferromag. Insul. works
   Domain wall chiral conduction observed
   Ferromagnetic TI at RT interface driven
   QAH state is yet to be reached

### **Custom Built Metal MBE**

Carl Zeiss Leo Supra 25



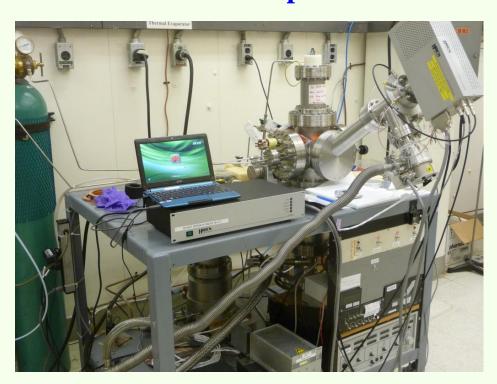
- 10 <sup>-10</sup> Torr, 14 sources, masks, plasma, insitu multilayers, sputtering,.... in-situ RHEED
- heating/cooling (80K to 1200K).....
- angled deposition nano structure creation

SEM (2nm)

Raith ebeam writing - nanopatterning (20nm features)

EDX – elemental analysis

# Nano patterning: Ion Miller with end point detector



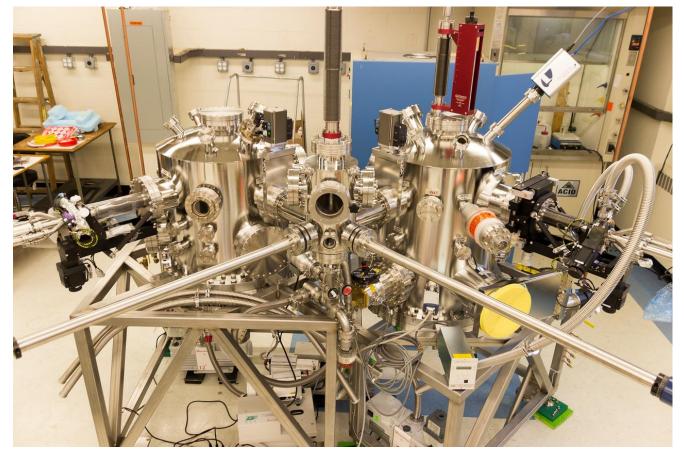
### Wire Bonder



Low temp cryostats down to 400 mK, 8 tesla SC magnet and electronics for transport measurements

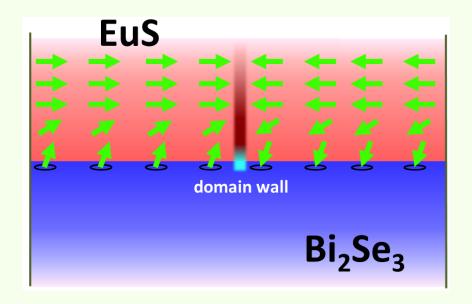
STM / c- AFM low temp probe, insitu sample transfer, 280 mK, 5 T in plane H (April 2015)

### New cluster MBE – The Water Molecule!

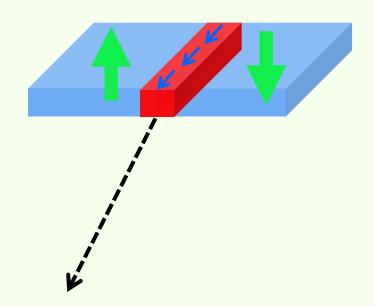


10<sup>-10</sup> torr, 27 Sources: K-cell, e-Gun evapn, Sputtering Heating/cooling (100K – 1200K), RHEED (*in situ structure*) Sample transferable in vacuum ('vacuum suitcase') Insitu masking, angled evaporation (nano devices) ....

### What happens at the interface:



 $Bi_2Se_3$  top surface at coercive field  $H_c$  (R minimum):

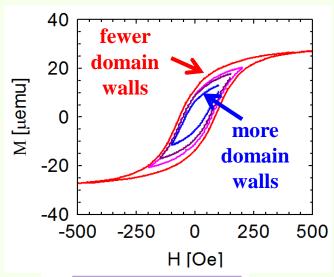


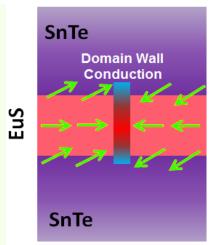
Chiral conduction channel in domain wall (unique in TI)

P. Wei et. al., PRL 110 (2013)

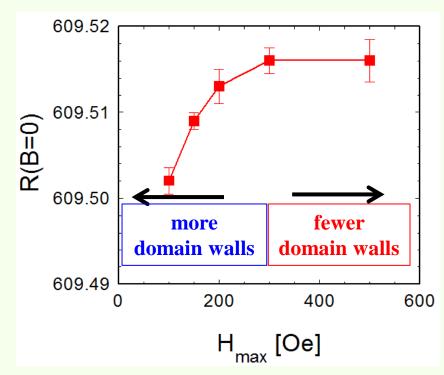
# Proximity induced magnetism in TCI SnTe: Tuning the Number of Domain Walls: the Minor Loop Regime

### **Minor loops of SnTe-EuS-SnTe Trilayer**





Resistance dependence on domain wall density at H = 0

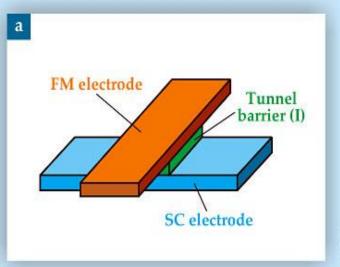


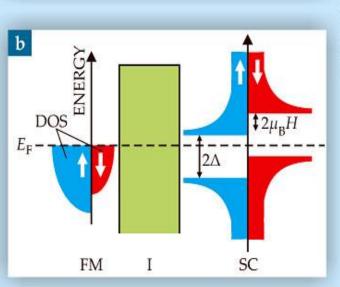
Magnetic domain walls enhance sample conduction

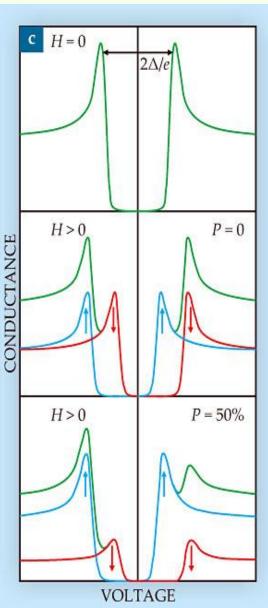
Correlation between magnetic domain structure and transport

Badih A. Assaf

### **Meservey – Tedrow Technique of Spin Polarized Tunneling**







SC / Insulator / Normal metal tunneling

Supercond. energy gap

In a magnetic field

Zeeman split states in SC

SC / Insulator / Normal metal tunneling

SC / Insulator / ferromagnet tunneling

**Tunneling e spin polarized** 

$$P = (n \uparrow - n \downarrow) / (n \uparrow + n \downarrow)$$

$$P = \frac{(Nv^2)_{\uparrow} - (Nv^2)_{\downarrow}}{(Nv^2)_{\uparrow} + (Nv^2)}$$